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COMPLEXES OF OSMIUM(III) DERIVED FROM O,O-DONOR LIGANDS

AHMED M. EL-HENDAWY

Chemistry Department, Faculty of Science, Damietta, Egypt

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Abstract—The complex $[Os^{III}Cl_3(PPh_3)_2MeOH]$ has been prepared and found to be a precursor for the synthesis of $[Os^{III}Cl_2(PPh_3)_2L]$ (L = monoanions of maltol, tropolone, acetylacetone, trifluoroacetylacetone, hexafluoroacetylacetone, benzoylacetone and dibenzoylmethane). These new complexes were characterized by spectroscopic measurements and exhibited a rich redox chemistry as demonstrated by cyclic voltammetry. The catalytic oxidation of alcohols in the presence of excess N-methylmorpholine-N-oxide by $[Os^{III}Cl_2(PPh_3)_2(acac)]$ has been studied and compared with that of the related ruthenium(III) complexes.

Mixed complexes of ruthenium(II) with triphenylphosphine and β-diketones, $[Ru(\beta\text{-diket})_2(PPh_3)_2]$, have been reported.[1] The low-spin ruthenium(III) complexes, $[RuX_2(\beta\text{-diket})(EPh_3)_2]$ (X = Cl, Br; E = P, As), have also been noted.[2,3] Recently,[4] we have prepared and characterized the complexes $[Ru^{III}Cl_2(PPh_3)_2L]$ (L = monoanions of maltol, kojic acid, tropolone and acetylacetone), but no work has so far been reported on similar complexes of osmium(III).

We now report the preparation of the new complexes $[Os^{III}Cl_2(PPh_3)_2L]$ [L = monoanions of maltol (malt), 3-hydroxy-2-methyl-4-pyrone; tropolone (trop), 2-hydroxy-2,4,6-cycloheptatrienone; acetylacetone (acac); trifluoroacetylacetone (tfacac); hexafluoroacetylacetone (hfacac); benzoylacetone (bac); and dibenzoylmethane (dbm)], starting with $[OsCl_3(PPh_3)_2MeOH]$. We also report their spectroscopic and electrochemical behaviour, together with the application of $[Os^{III}Cl_2(PPh_3)_2(acac)]$ to the catalytic oxidation of alcohols in the presence of N-methylmorpholine-N-oxide (NMO) as co-oxidant, since the analogous ruthenium(III) complex[4] and also the $Ru^{II}Cl_2(PPh_3)_3$/NMO system have been studied in this way.[5,6]

RESULTS AND DISCUSSION

On attempting to prepare *fac*-$[OsCl_3(PPh)_3]$ by the method of Taqui Khan *et al.*[7] using $Na_2[OsCl_6]$ instead of $(NH_4)_2[OsCl_6]$, a yellow solid was isolated and shown to be $[OsCl_3(PPh_3)_2MeOH]$ after recrystallization from methanol. Its IR spectrum has a strong broad band at 3473 cm^{-1} likely to have arisen from the ν(O—H) vibration, medium intensity bands at 2984 and 2911 cm^{-1} probably due to ν(C—H), and strong ones at 906 and 889 cm^{-1} which are attributed to the ν(C—O) of coordinated MeOH in the complex. These bands are absent both in $[RuCl_2(PPh_3)_3]$ and our present complexes $[OsCl_2(PPh_3)_2L]$ (L = O,O-donor ligand). We have also prepared $[RuCl_3(PPh_3)_2MeOH]$[8] and observed similar IR bands at 3505, 2941, 2836 and 1012 cm^{-1}, compared with those reported for $[RuCl_3(AsPh_3)_2MeOH]$[9] at 3480 and 1010 cm^{-1}.

Reaction of $[OsCl_3(PPh_3)_2MeOH]$ (**I**) with the O,O-donor ligands (HL) by refluxing for 0.5–2.5 h in methanol affords nice microcrystals with yields of 20–65%. Analytical data indicate that complexes have the formula $[OsCl_2(PPh_3)_2L]$ (L = malt, trop, acac, tfacac, hfacac, bac or dbm). These complexes are only soluble in CH_2Cl_2 and their molar conductivities are very low. Refluxing complex **I** alone in CH_3CN for a few hours gave a red solution from which red crystals were isolated. Analytical data were consistent with this being $[OsCl_3(PPh_3)_2CH_3CN]$, which was previously[10] prepared by long reflux of *trans*-$[OsCl_4(PPh_3)_2]$ in CH_3CN. Dissolution of **I** in CH_2Cl_2 and concentration of the solution by heating yields $[OsCl_3(PPh_3)_2CH_2Cl_2]$ as brown crystals.

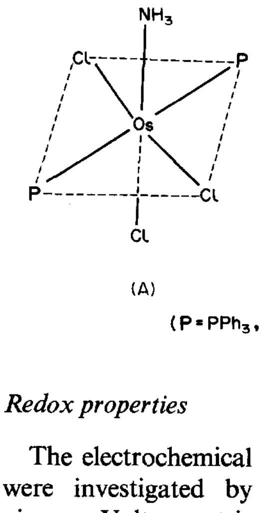
The IR spectra of the complexes showed all the bands due to triphenylphosphine and coordinated L. The general features are similar to those observed for analogous ruthenium complexes.[2-4] Characteristic bands of L are slightly shifted to lower wavenumbers; e.g. the band in the region 1555–1510 cm^{-1} for $[MCl_2(PPh_3)_2L]$ (M = Ru,[4] L = malt, trop, acac) was found at 1549–1510 cm^{-1} (M = Os). This band is tentatively assigned to $\nu(C{=}O)$, where a bathochromic shift (75–105 cm^{-1}) for the carbonyl groups upon coordination is expected.[11,12] A strong band attributed to $\nu(C{-}O)$ was found around 1350 cm^{-1} for $[OsCl_2(PPh_3)_2L]$ (L = trop, acac, bac, dbm), similar to those observed for analogous ruthenium complexes[4] and for $W_2O_5(trop)_2$.[13] The trifluoro- and hexafluoroacetylacetonato complexes show strong bands at 1296 and 1257 cm^{-1}, respectively, also arising from $\nu(C{-}O)$ vibrations. Only one band around 315 cm^{-1} has appeared in the $[OsCl_2(PPh_3)_2L]$ complexes, this is likely to be due to $\nu(Os{-}Cl)$.[14,15] This band is shifted to lower wavenumber in the osmium complexes compared with that observed near 335 cm^{-1} for ruthenium complexes.[4] The most important IR bands are listed in Table 1; the deep colours of the complexes make them unsuitable for Raman studies.

Magnetic susceptibility measurements for $[OsCl_3(PPh_3)_2MeOH]$ at room temperature showed a magnetic moment, μ_{eff}, of 1.48 BM corresponding to one unpaired electron. The other complexes $[OsCl_2(PPh_3)_2L]$, however, have μ_{eff} close to the spin-only value of one unpaired electron lying in the range 1.7–2.0 BM (Table 2), similar to those of *mer*- and *fac*-$[OsL'_3X_3]$ ($L' = PBu^n_2Ph$, PPr^n_2Ph, PPr^n_3; X = Cl, Br).[16] This suggests the low-spin d^5 $(t_2g)^5$ configuration for the osmium(III) ion in an octahedral environment, which is also the case for the analogous ruthenium(III) complexes.[4]

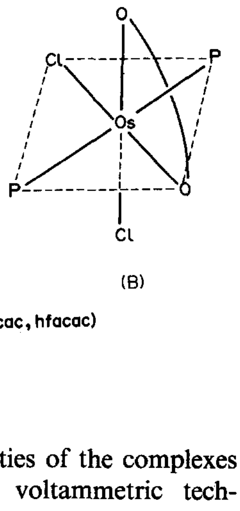
Electronic spectra and electron spin resonance

The UV–vis spectra of complexes in CH_2Cl_2 solution (Table 1) showed a broad band around 550 nm of low molar absorptivity ($\varepsilon = 500\ M^{-1}\ cm^{-1}$) compared with those for analogous ruthenium(III) complexes[4,17,18] which have been observed at 600 nm. This band may owe its origin to a *d–d* transition. In $[OsCl_2(PPh_3)_2L]$ complexes (L = malt, trop), the band at 550 nm is replaced by high intensity bands in the region 700–500 nm which are tentatively assigned to the $\pi(O,O\ donor) \rightarrow t_2(Os^{III})$ transition, while the weaker ligand-field bands may be obscured by such transitions. Similar bands also were found for $[Os(bipy)_2(acac)]^{2+}$ and $[RuCl_2(bipy)(acac)]$ at 530 nm ($\varepsilon = 1500$).[19] The strong bands in the 400 nm region or below could arise from $Cl \rightarrow t_2$ transitions.[14,19]

The ESR spectra in CH_2Cl_2 frozen glasses of the complexes (concentration 5×10^{-3} M) were carried out at −170°C. Cooling was by means of cold nitrogen gas passed over the sample tube. The most significant spectra are those of $[OsCl_2(PPh_3)_2L]$ (L = acac, hfacac). The acetylacetone complex [Fig. 1(a)] shows only two peaks, $g_x = 2.96$ and $g_y = 1.59$, while the third component, g_z, is presumably very low (< 0.46) and lies beyond the maximum field obtainable ($B_z > 1400$ G). This is typically in accordance with the ESR spectrum of polycrystalline *mer*-$[OsCl_3(PBu^n_2Ph)_3]$ which has *g* values of 3.3, 1.65 and 0.36 in C_{2v} symmetry.[20] The hexafluoroacetylacetonate complex has another type of ESR spectrum [see Fig. 1(b)] with $g_x = 3.00$, $g_y = 1.63$ and $g_z = 1.53$, similar to that of $[RuCl_3(PBu^n_2Ph_3)_2]$[20] but with closer peaks (g_y and g_z). The X-ray crystal structure of $[OsCl_3(NH_3)(PPh_3)_2]$ (**A**)[21] has a distorted octahedral configuration with the movement of Cl atoms *cis* to N towards the nitrogen atom. A similar structure (**B**) for our compounds of C_2 symmetry is expected as shown below.



(A)



(B)

(P = PPh_3, O–O = acac, hfacac)

Redox properties

The electrochemical properties of the complexes were investigated by cyclic voltammetric techniques. Voltammetric half-potential vs the Ag electrode for 0.1 M $Bu^n_4NPF_6$–CH_2Cl_2 solutions are presented in Table 2. The voltammogram reveals a pair of cathodic and anodic peaks in each case which correspond to Os^{III}/Os^{II} reduction and Os^{III}/Os^{IV} oxidation, respectively, and the peak separation (ΔE) for each complex is close to that anticipated for a Nernstian one-electron process (59 mV).[22] For $[OsCl_2(PPh_3)_2(acac)]$, a representative example (Fig. 2) compared with that of ferrocene [$E_{1/2} = 0.21$ V, $\Delta E = 50$ mV) under the same conditions, shows a quasi-reversible one-electron oxidation wave, $E_{1/2} = 0.78$ V, $\Delta E = 70$ mV, and of another wave reduction of $E_{1/2} = -0.56$ V and $\Delta E = 80$ mV.

Table 1. Analytical and spectroscopic data for complexes

Compound	Colour	Time of reflux, h (Yield)	Analysis, Found (Calc), % C	H	IR data, wavenumbers (cm^{-1}) ν(C═O)	ν(C—O)	ν(Os—Cl)	Other bands	UV–vis data, λ_{max}, nm (ε, M^{-1} cm^{-1})
$[OsCl_3(PPh_3)_2MeOH]$	Yellow	4 (80)	52.9 (52.1)	4.0 (4.0)			306s	2984m, 2911w, 906s, 889s	692 (220), 490sh (541), 375 (3,050), 353 (2,800), 337 (2,700), 287sh (8,560), 260sh (18,000)
$[OsCl_2(PPh_3)_2(malt)]$	Green	0.6 (55)	54.7 (54.4)	3.9 (3.8)	1549s	—	310m		606 (1,080), 417 (3,380), 317 (8,060), 274 (12,200), 235 (52,420)
$[OsCl_2(PPh_3)_2(trop)]$	Deep brown	0.5 (50)	57.1 (56.9)	3.9 (3.9)	1510s	1347s	312m		713 (592), 654 (742), 558 (1,274), 486 (3,316), 423 (8,000), 332 (13,880), 315 (14,780), 235 (58,800)
$[OsCl_2(PPh_3)_2(acac)]$	Brown–red	0.5 (65)	55.6 (55.6) Cl : 7.9(8.0)	4.2 (4.2)	1519s	1367s	326m		558 (602), 449 (1,014), 363 (3,344), 354 (3,900), 294 (7,580), 277 (9,220), 268 (9,960), 234 (48,000)
$[OsCl_2(PPh_3)_2(tfacac)]$	Orange	2.5 (30)	52.2 (52.4)	3.6 (3.6)	1522s	1296s	321s		533 (426), 437 (1,914), 382 (4,140), 299 (7,620), 276 (8,760), 269 (9,400), 234 (46,840)
$[OsCl_2(PPh_3)_2(hfacac)]$	Brown	2.0 (35)	47.8 (47.2)	3.1 (3.1)	1447s	1257s	325m		533 (488), 461 (2,150), 421 (3,228), 417 (3,920), 309 (7,220), 276 (7,800), 268 (8,940), 234 (46,040)
$[OsCl_2(PPh_3)_2(bac)]$	Green	1.5 (15)	58.1 (58.3)	4.1 (4.1)	1550s 1520s	1359s	314m		580 (596), 313 (12,840), 233 (49,540)
$[OsCl_2(PPh_3)_2(dbm)]$	Green	1.5 (30)	60.7 (60.7)	4.1 (4.1)	1520s	1358s	318m		578 (532), 341 (18,100), 260 (29,860), 233 (55,240)
$[OsCl_3(PPh_3)_2CH_3CN]$	Red	2.0 (50)	52.7 (52.9) N : 1.65(1.6)	3.8 (3.8)			314m		
$[OsCl_3(PPh_3)_2CH_2Cl_2]$	Brown		49.6 (49.0)	3.5 (3.5)			323s		
$[RuCl_3(PPh_3)_2MeOH]$	Green							2941w, 2836w, 1012m	

Table 2. Magnetic moments and voltammetric half-wave potentials of the complexes

Complex	μ_{eff} (BM)	$E_{1/2}$ (reduction)	ΔE (V)	$E_{1/2}$ (oxidation)	ΔE	$E_{p,a}$[a]	Scan rate ($mV\ s^{-1}$)
$[OsCl_3(PPh_3)_2MeOH]$	1.48	−0.76	0.070	+0.29	0.060		50, 100
$[OsCl_2(PPh_3)_2(malt)]$	1.74	−0.57	0.070	+0.59	0.240		10, 20, 50
$[OsCl_2(PPh_3)_2(trop)]$	1.66	−0.47	0.070	+0.63	0.250		20, 50, 100
$[OsCl_2(PPh_3)_2(acac)]$	1.89	−0.56	0.080	+0.78	0.070		20, 50, 100
$[OsCl_3(PPh_3)_2(tfacac)]$	2.01	−0.44	0.080	+0.94	0.080		10, 20, 50
$[OsCl_2(PPh_3)_2(hfacac)]$	1.92	−0.21	0.080	+1.21	0.060		10, 20, 50
$[OsCl_2(PPh_3)_2(bac)]$		−0.69	0.100	+0.64	0.080		10, 20, 50
$[OsCl_2(PPh_3)_2(dbm)]$	1.72	−0.66	0.080	+0.64	0.080		20, 50, 100
$[RuCl_2(PPh_3)_2(acac)]$		−0.41	0.070	—	—	+1.26	

[a] Corresponding anodic peak of oxidation.

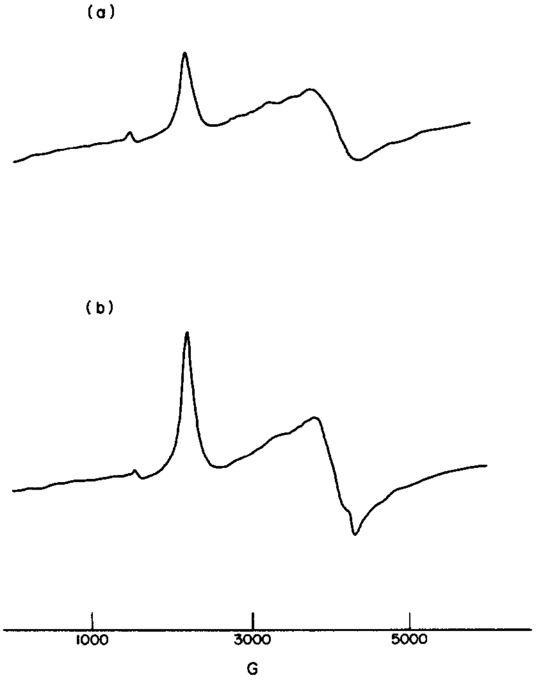


Fig. 1. (a) ESR spectra of *trans*-$[OsCl_2(PPh_3)_2(acac)]$; (b) ESR spectra of *trans*-$[OsCl_2(PPh_3)_2(hfacac)]$.

For scan rates (SR) between 10 and 100 mV s^{-1}, the ratio $i_p/(SR)^{1/2}$ (i_p = peak current) was constant and the ratio of the anodic to cathodic peak current is one, the peak separation being independent of the scan rate. This indicates that electron transfer is reversible or approaches reversibility and the mass transfer is limited. In tropolonato and maltolato complexes, the peak separation of the oxidation wave is 240–250 mV, indicating irreversible behaviour. The presence of such oxidation and reduction waves seems to be typical of osmium(III) halide complexes, e.g. $[OsCl_3(PPh_3)_2(CH_3CN)]$, $[OsCl_3(py)_2(PPh_3)]$[10] and $[Os^{III}X_2(PPh_3)_2L]$[23] (X = Cl, Br; HL = 2-hydroxypyridine, 2-hydroxy-6-methylpyridine and picolinic acid). From Table 2 which includes the cyclic voltammetric data, we conclude that $E_{1/2}$ of the reduction wave is shifted to lower or more negative values relative to $[OsCl_2(PPh_3)_2(acac)]$, reflecting an increase of basicity with more negative values of $E_{1/2}$ as the O,O-donor ligand changes in the order

$$\text{hfacac} < \text{tfacac} \simeq \text{trop} < \text{acac} \simeq \text{malt} < \text{dbm} \simeq \text{bac}.$$

There is thus an anticipated increase in the ease of oxidization and decrease in the ease of reduction for the complexes containing benzoylacetone or dibenzoylmethane ligands. The stabilities of the Os^{IV}, Os^{III} and Os^{II} oxidation states in these complexes is reflected by the reversibility of these processes:

$$[OsCl_2(PPh_3)_2L]^+ \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [OsCl_2(PPh_3)_2L] \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [OsCl_2(PPh_3)_2L]^-.$$

Catalytic oxidations

Since $[RuCl_2(PPh_3)_2(acac)]$[4] has been used in the presence of excess NMO for the catalytic oxidation of primary alcohols to aldehydes and secondary alcohols to ketones we tried to use $[OsCl_2(PPh_3)_2(acac)]$ (**II**) as an oxidation catalyst. Although it did catalytically oxidize *p*-methoxybenzyl alcohol to the aldehyde and α-tetralol to α-tetralone over 15 and 36 h, respectively, the yields were low (12 and 18%, respectively, with catalytic turnovers of 50) while piperonyl alcohol and benzohydrol were not oxidized at all. The low reactivity of the osmium

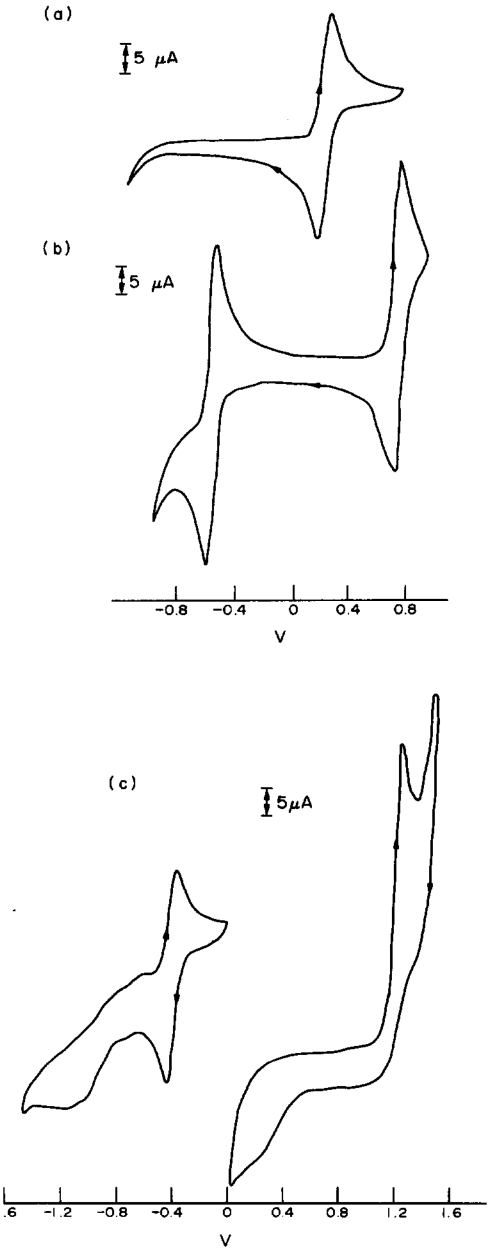


Fig. 2. Cyclic voltammogram, in CH_2Cl_2 with 0.1 M $(Bu^n{}_4N)PF_6$ as supporting electrolyte; volts vs Ag electrode, scan rate 100 mV s^{-1}: (a) Ferrocene; (b) *trans*-$[OsCl_2(PPh_3)_2(acac)]$ ($\sim 10^{-3}$ M), scan rate 50 mV s^{-1}; (c) *trans*-$[RuCl_2(PPh_3)_2(acac)]$ ($\sim 10^{-3}$ M).

complex in comparison with its ruthenium analogue is perhaps not surprising, thus $[RuO_4]^-$ is a much better oxidant than $[OsO_4]^-$.[24] In connection with the effectiveness of $[RuCl_2(PPh_3)(acac)]$ as an oxidant it is of interest to note that an extension of our earlier[4] cyclic voltammetric work on $[RuCl_2(PPh_3)_2(acac)]$ (**III**) to more positive potentials shows a further irreversible oxidation peak ($E = +1.26$ V) of height three times greater than the reduction wave at $E_{1/2} = -0.41$ V ($\Delta E = 70$ mV) vs Ag electrode. The latter wave is due to the Ru^{III}/Ru^{II} reduction,[4] so that the oxidation peak at 1.26 V probably arises from oxidation of Ru^{III} to Ru^{VI}; such an oxidation peak is not found for $[OsCl_2(PPh_3)_2(acac)]$, which gives only Os^{III}/Os^{IV} oxidation. This supports our earlier suggestion[4] that oxidations effected by **III** are likely to occur via higher oxidation states of ruthenium. It is also relevant that $[Ru(acac)_3]$, which has a similar cyclic voltammogram[4,25] to that of **II**, does not effect oxidations of alcohols in the presence of NMO.

EXPERIMENTAL

Preparation of complexes

All preparations use $[OsCl_3(PPh_3)_2MeOH]$ as starting material. This was prepared as follows; a solution of $Na_2[OsCl_6]\cdot 3H_2O$ (0.45 g, 0.9 mmol) in 2-methoxyethanol (60 cm^3) was degassed by passing N_2 through, then conc. HCl (30 cm^3) was added. The mixture was refluxed for 30 min. To the hot solution was added a solution of triphenylphosphine (1.0 g, 3.8 mmol) in 2-methoxyethanol (10 cm^3) and refluxing was continued for 3–4 h under nitrogen. The volume was reduced by 75% and the remaining solution was stored in a refrigerator overnight. After addition of methanol (50 cm^3) the solution was heated and cooled again, when a yellow solid appeared, which was washed thoroughly with water, methanol and ether. The product was recrystallized from methanol and dried *in vacuo*.

Preparation of $[OsCl_2(PPh_3)_2(acac)]$. The complex $[OsCl_3(PPh_3)_2MeOH]$ (0.42 g, 0.5 mmol) was dissolved in methanol (80 cm^3) and refluxed for 30 min on a steam bath until the solution became slightly dark yellow. Distilled acetylacetone (1 cm^3) was then added. A reddish-brown solution was obtained and after continuing reflux for another 30 min, nice brown crystals precipitated which were filtered off, washed with methanol and ether, and dried *in vacuo*.

Preparation of $[OsCl_2(PPh_3)_2L]$ (L = malt, trop, tfacac, hfacac, bac, dbm). A solution of $[OsCl_3(PPh_3)_2MeOH]$ (0.42 g, 0.5 mmol) in methanol (80 cm^3) was refluxed for 30 min, followed by the addition of the ligand (HL) (0.9 mmol). The mixture was refluxed for an appropriate time (as in Table 1). Nice microcrystals formed, which were filtered off, washed with a little methanol and ether and finally dried *in vacuo*. Analytical data are given in Table 1.

Catalytic oxidation by $[OsCl_2(PPh_3)_2(acac)]$ **(II)**

The oxidation of *p*-methoxybenzyl alcohol is typical. To a solution of *p*-methoxybenzyl alcohol (1 mmol) was added NMO (3 mmol) in CH_2Cl_2 (20 cm^3) and 2×10^{-2} mmol of compound **II**. The solution was stirred for 15 h in the presence of 4 Å molecular sieves (0.5 g). The mixture was evaporated to dryness and extracted with ether (2×25 cm^3). The combined ethereal extracts were filtered and evaporated to give *p*-methoxybenzaldehyde which was characterized and quantified as its 2,4-dinitrophenylhydrazone derivative.

The same experiment was carried out using $[Ru(acac)_3]$ (prepared by the literature method[26]) in place of **II** above. The red solution of the reaction mixture does not change and there was no oxidation.

IR spectra were measured on a Perkin–Elmer FT 1720 instrument as liquid paraffin mulls between CsI plates and as KBr discs. The electronic spectra were measured on a Philips PU 8740 UV–vis spectrophotometer or Varian 634 model. ESR spectra were recorded with a Varian E-12 spectrometer. Cyclic voltammetric studies were carried out on a potentiostat/generator (Oxford Electrodes) using a platinum working electrode and silver reference electrode in conjunction with a Philips PM 8043 X–Y recorder. Magnetic measurements were made on a Johnson Matthey magnetic susceptibility balance.

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